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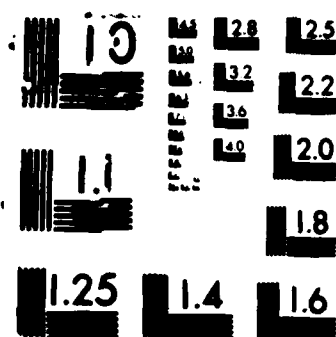
CONDUCTANCE OF AQUEOUS SOLUTIONS OF
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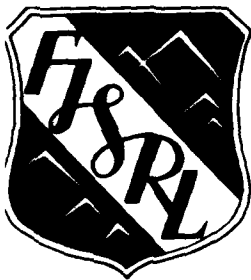




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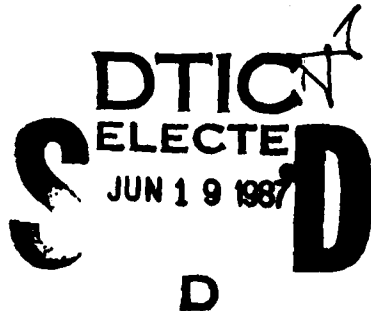
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FRANK J. SEILER RESEARCH LABORATORY

CONDUCTANCE OF
AQUEOUS SOLUTIONS OF
1-METHYL-3-ETHYLIMIDAZOLIUM
CHLORIDE

Chester J. Dymek, Jr.

JUNE 1987



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<p>The specific conductance and pH of aqueous solutions of 1-methyl-3-ethylimidazolium chloride (MEICl) were measured at room temperature. The behavior of MEICl is characteristic of a strong electrolyte. The transport numbers of MEI^{+} and Cl^{-} calculated from single ion equivalent conductances at infinite dilution were $t_{+}(MEI^{+}) = 0.29$ and $t_{-}(Cl^{-}) = 0.71$. <i>(Keywords: -)</i></p>			
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Preface

The formation of room temperature molten salts from mixtures of 1-methyl-3-ethylimidazolium chloride (MEICl) and AlCl_3 strongly suggests that MEICl is a salt. However, several attempts at formation of MEICl crystals had not been successful, so the nature of the MEICl structure in general and the MEI-Cl bond in particular remained open to question. The conductance and pH behavior of aqueous MEICl appeared to be a reasonable way of determining how readily it dissociates into ions, i.e., how strong an electrolyte it is, and other questions on the salt character of MEICl. I wish to thank Fred Kibler for assistance in repair of the conductance cells and Missy Landess for word processing this report.



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Introduction

Mixtures of 1-methyl-3-ethylimidazolium chloride (MEICl) and AlCl_3 are ionic liquids at room temperature. These melts are known to have appreciable conductivities and are of interest both as electrolytes and nonaqueous reaction media (1,2). Melt properties are generally strongly dependent on the stoichiometric mole fraction of AlCl_3 in the melt, i.e., $N = \text{mol}(\text{AlCl}_3) / [\text{mol}(\text{AlCl}_3) + \text{mol}(\text{MEICl})]$. The transport numbers of the ions in basic melts (which have N less than 0.5 and contain Cl^- , a Lewis base, and AlCl_4^-) have been determined (3). The value of $t_+(\text{MEI}^+)$ is virtually constant at 0.70 over the range $0.33 < N < 0.50$, while $t_-(\text{Cl}^-)$ and $t_-(\text{AlCl}_4^-)$ vary in roughly linear fashion on their concentration and $t_-(\text{Cl}^-) + t_-(\text{AlCl}_4^-) = 0.30$. Similar behavior has also been reported in acidic melts ($N > 0.5$) with $t_+(\text{MEI}^+) = 0.71$ (4).

The unexpectedly high t_+ for MEI^+ in these melts has not been adequately explained. In fact, the ionic associations in the melts and the melt structure in general are still subject to varied interpretations (5) (6). In this work, conductivities of aqueous solutions of MEICl were studied as a means of forming a baseline picture of MEICl as an electrolyte apart from AlCl_3 .

Experimental

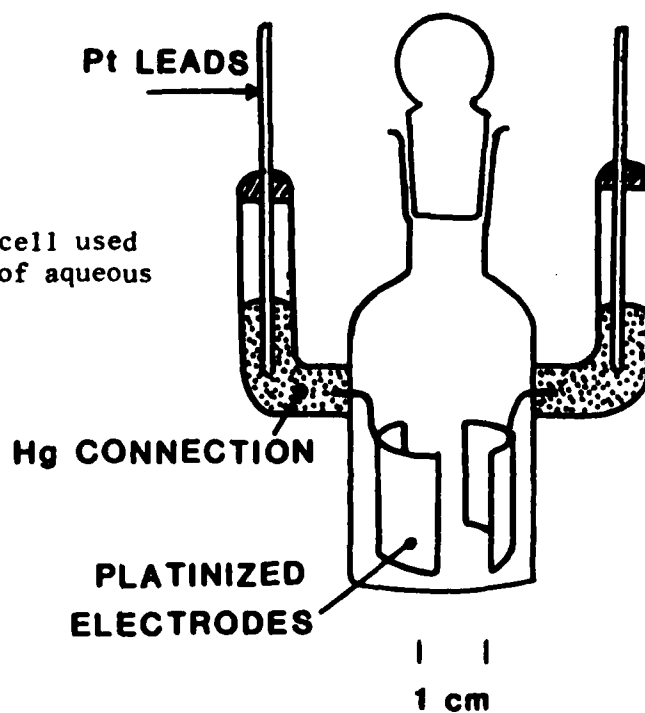
MEICl was prepared as previously described (7). Aqueous solutions were prepared by addition of MEICl to conductivity water (18.3 M Ω) obtained using a SYBRON Barnstead Glass Still with a NANOpure filter. Successive dilutions were made in 200 ml volumetric flasks. Conductance measurements were made using a YSI Model 31 conductivity bridge and two conductance cells of the type illustrated in Fig. 1. A variable capacitance of up to 1 μF was used to balance cell capacitance as needed. Measurements were all made at 1000 Hz AC. The cell constants were determined to be $0.132 \pm 0.001 \text{ cm}^{-1}$ and $0.195 \pm 0.002 \text{ cm}^{-1}$ at 25°C using 0.0200N KCl solution. The cells were maintained at $25.0 \pm 0.1^\circ\text{C}$ by immersion in a circulating bath.

The pH of aqueous solutions of MEICl was measured at 21°C using a Beckman Zeromatic SS-3 pH meter. Dilutions of the prepared 0.307 M MEICl solution were made with a 100 ml volumetric flask and a graduated cylinder. Conductivity water from the Barnstead Glass Still was used for these solutions.

TABLE 1.

Table 1. Run ID	M(MEICl) mol/L	Equivalent Conductance, S-cm ² /eq	M(MEICl) (mol/L) ¹	Specific Conductance, S/cm
6:B	.000195	107.3	.014	.000021
5:B	.000391	105.9	.02	.000041
6:B	.000391	105	.0198	.000041
5:B	.000781	105	.028	.000082
6:B	.000781	104.2	.028	.000081
5:B	.001563	103.2	.04	.00016
6:B	.001563	102.8	.0395	.000161
5:B	.003125	101	.056	.00032
6:B	.003125	100.9	.0559	.000315
5:B	.00625	97.6	.079	.00061
6:B	.00625	96.3	.0791	.000602
5:B	.0125	94.3	.112	.00118
6:B	.0125	94.6	.112	.00118
5:B	.025	91.4	.158	.00228
6:B	.025	91.2	.158	.00228
4:A	.05	85.7	.224	.00429
5:B	.05	87.3	.224	.00436
6:B	.05	87.9	.224	.00439
4:A	.1	84.8	.316	.00848
6:B	.1	82.4	.316	.00824
4:A	.125	81.3	.354	.0102
4:A	.2	76.2	.447	.0152
4:A	.2	77	.447	.0154
6:B	.2	67.8	.447	.0136
4:A	.25	69.6	.5	.0174
6:B	.4	61	.632	.0244
4:A	.5	54.9	.707	.0275

Figure 1. Conductivity cell used to measure conductance of aqueous MEICl solutions.



Results and Discussion

The concentrations and specific conductances of the aqueous MEICl solutions measured are given in Table I. A plot of equivalent conductance vs. concentration is shown in Fig. 2. Comparison of the MEICl curve with those for KCl and acetic acid show that MEICl should be characterized as a strong electrolyte, readily dissociating in water.

A plot of equivalent conductances vs. \sqrt{c} is shown in Fig. 3 for very dilute solutions. Comparison with the plots for KCl and acetic acid make it even more evident that MEICl completely dissociates in water. The linear dependence confirms that MEICl is a strong electrolyte and provides a value for Λ_0 , the equivalent conductance at infinite dilution. A least squares fit of the points for very dilute solutions as shown in Fig. 4 gives $\Lambda_0 = 107.8 \pm 0.5 \text{ S cm}^{-1}$ at 25°C. Given the value of $\lambda_0(\text{Cl}^-)$ at 25°C in aqueous solution of 76.3 S cm^{-1} (), a value for $\lambda_0(\text{MEI}^+)$ of 31.5 S cm^{-1} is obtained.

From these values for λ_0 , a transport number for MEI^+ in aqueous solution can be obtained from

$$t_+ = \frac{\lambda_0 +}{\lambda_{0+} + \lambda_{0-}}$$

The $t_+(\text{MEI}^+)$ of 0.29 and $t_-(\text{Cl}^-)$ of 0.71 obtained are significantly different, as expected, from their values in the MEICl/ AlCl_3 melts. Here the transport numbers and mobilities of the ions are related to their cross sections, or hydrodynamic radii, whereas in the melts, the complex ionic structure and interactions determine ion mobilities.

As a strong electrolyte MEICl is almost certain to have an ionic crystal lattice in the solid state. However, many previous attempts to recrystallize MEICl prepared using the reported synthesis (7) were unsuccessful. Recently a new preparative process involving recrystallization out of acetonitrile has produced crystals of MEICl. Efforts are underway to obtain their structure by X-ray diffraction.

To insure that no other ions (H_3O^+ or OH^-) were present in aqueous MEICl in significant concentrations to affect conductance, pH measurements were made. A 0.307 M MEICl solution had a pH of 8.40. This amounts to $[\text{OH}^-] = 2.5 \times 10^{-6} \text{ M}$, which is five orders of magnitude less than the MEI^+ and Cl^- concentrations. It can thus be assumed that all the conductance in the MEICl solutions is due to MEI^+ and Cl^- ions. The slightly basic character of these solutions is probably due to the presence in the MEICl of small amounts of the

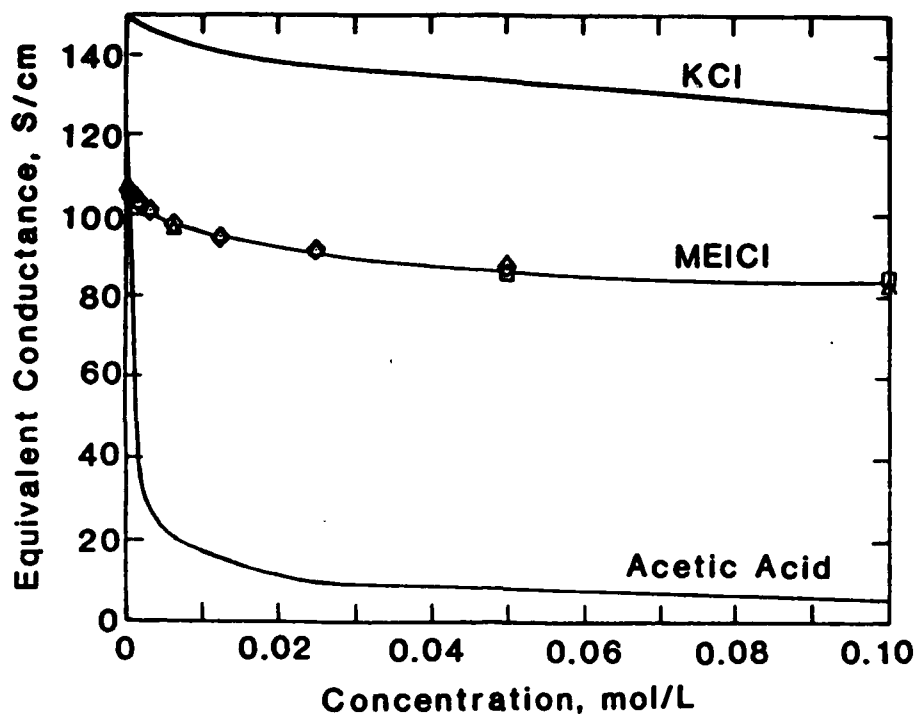


Figure 2. Plot of equivalent conductance vs. concentration of MEICl in aqueous solution. Plots of KCl and acetic acid shown for comparison are from Ref. 8, Ch II.

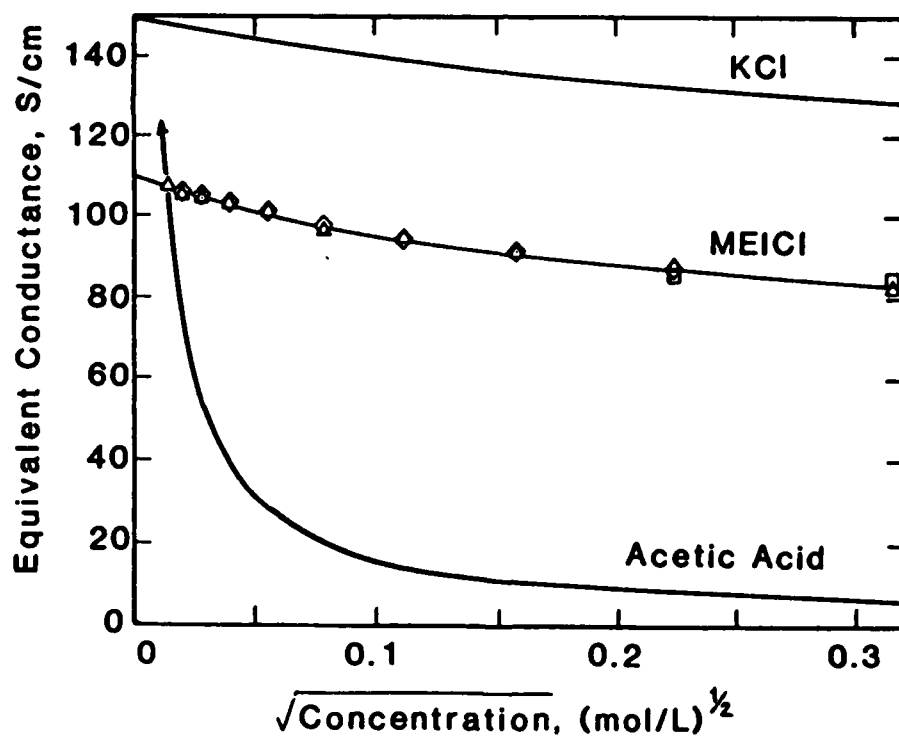


Figure 3. Plot of equivalent conductance vs. square root of concentration of MEICl in aqueous solution. Plots of KCl and acetic acid shown for comparison are from Ref. 8, Ch II.

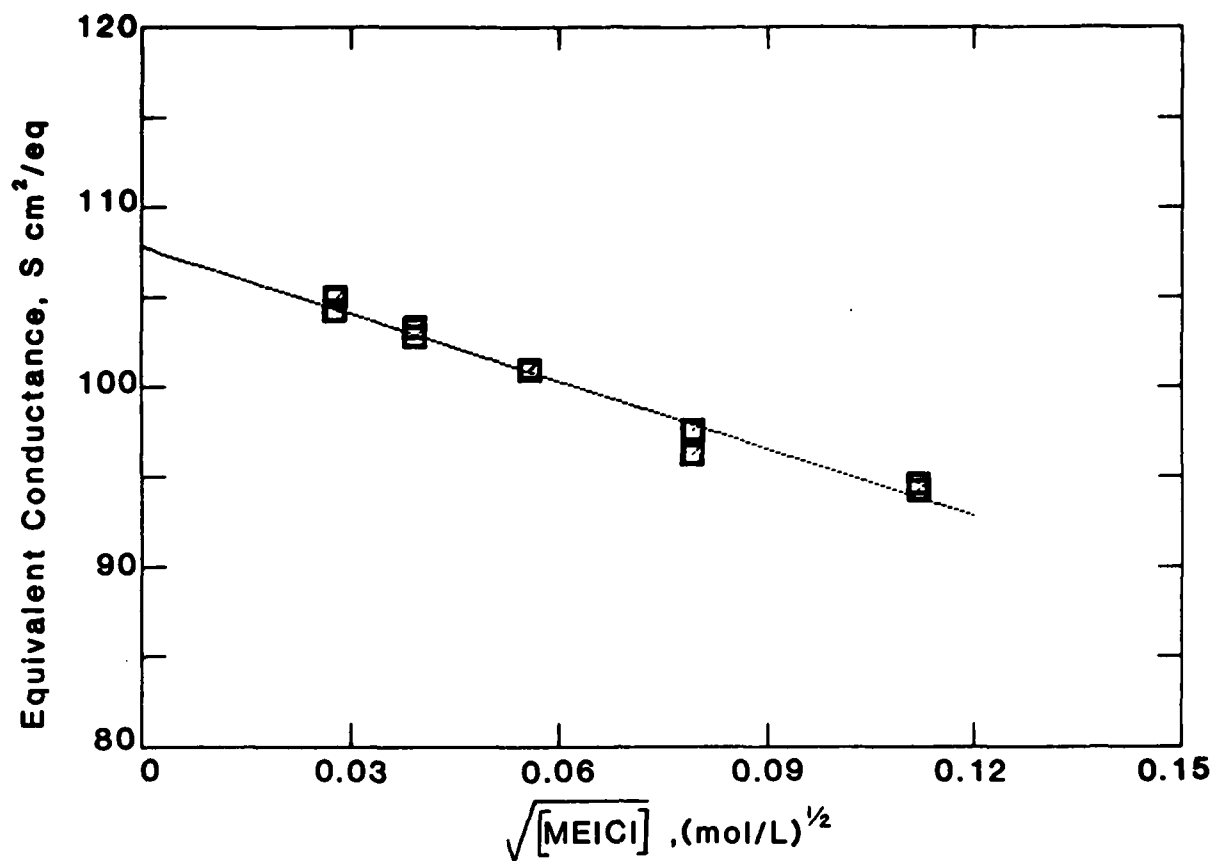


Figure 4. Least squares fit of equivalent conductance to square root of concentration in very dilute aqueous solutions of MEICl.

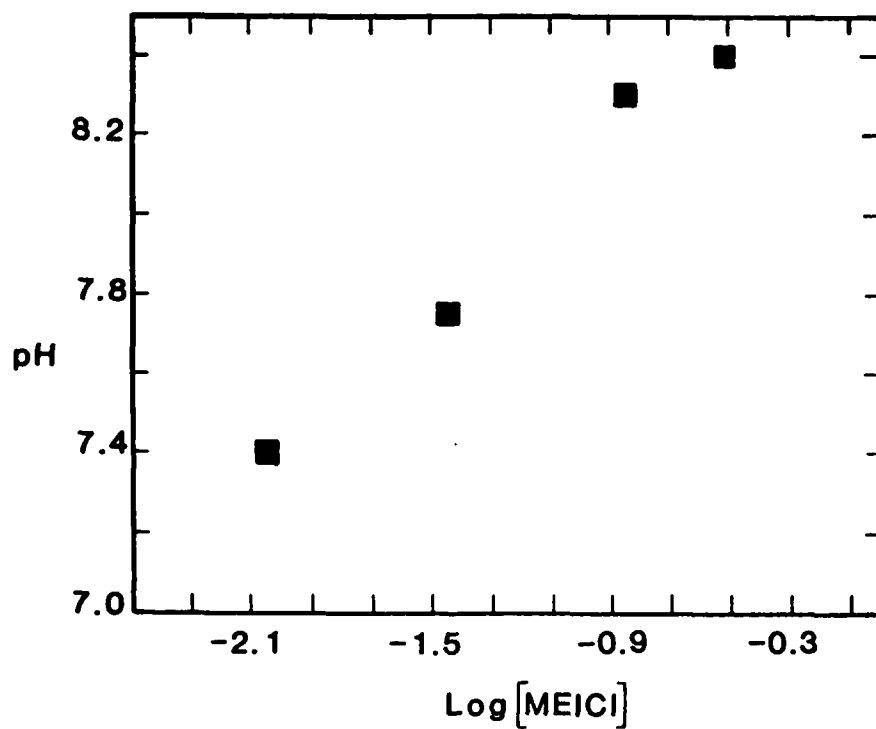


Figure 5. pH of aqueous MEICl solution vs. log of molarity of MEICl.

unreacted base, methylimidazole, as an impurity. As the solution was diluted, the pH decreased in an approximately linear fashion with $\log [\text{MEICl}]$ (See Fig. 5). Thus it appears that this base is fully protonated at the concentrations at which it is present in the MEICl solutions studied.

Conclusions

Conductance measurements of aqueous MEICl solutions show that MEICl is a strong electrolyte, implying an ionic crystal lattice for the solid state. The equivalent conductance at infinite dilution is $107.8 \pm 0.5 \text{ S cm}^2/\text{eq}$. The transport numbers of MEI^+ and Cl^- in water were found to be 0.29 and 0.71 based on single ionic equivalent conductances. This is just the reverse of the transport numbers in $\text{MEICl}/\text{AlCl}_3$ melts ($t_+ (\text{MEI}^+) = 0.70$).

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